

## **DEVELOPMENT ENHANCEMENT OF RADIATION-SENSITIVE ELEMENTS**

### **Field of the Invention**

- 5     The invention pertains to the field of radiation-sensitive compositions and, in particular, to their use in lithography.

### **Background of the Invention**

- 10    Lithographic processes involve establishing image (printing) and non-image (non-printing) areas on a substrate, substantially on a common plane. When such processes are used in printing industries, non-image areas and image areas are arranged to have different affinities for printing ink. For example, non-image areas may be generally hydrophilic or oleophobic and image areas may be oleophilic.

- 15    The types of electronic parts whose manufacture may use a radiation-sensitive composition include printed wiring circuit boards, thick-and thin-film circuits, comprising passive elements such as resistors, capacitors and inductors; multichip devices; integrated circuits; and active semiconductor devices. The electronic parts may suitably comprise conductors, for example copper board; semiconductors, for  
20    example silicon, or germanium or Group III-V compound materials; and insulators, for example silica, as a surface layer with silicon beneath, with the silica being selectively etched away to expose portions of the silicon beneath. In relation to masks, a required pattern may be formed in the coating on the mask precursor, for example a plastics film, which is then used in a later processing step, in forming a pattern on, for  
25    example, a printing or electronic part substrate.

- Conventionally, laser direct imaging methods (LDI) have been known which directly form an offset printing plate or printed circuit boards on the basis of digital data from a computer. LDI offers the potential benefits of better line quality, just-in-time  
30    processing, improved manufacturing yields, elimination of film costs, and other recognized advantages. Examples of such methods include: (1) an electrophotographic method, (2) a photopolymerization method based on the combination of exposure by an Argon laser and post-heating, (3) a method in which a silver salt sensitive material is deposited on a photosensitive resin, (4) a method using  
35    a silver master and (5) a method in which a silicone rubber layer is decomposed by

discharge breakdown or a laser beam.

However, in the electro-photographic method (1), processing such as charging, exposure and development are complicated, and the device used for the processing is complex and large. In method (2), a post-heating step is required. Further, a highly sensitive plate material is also required, and handling thereof in a light room is difficult. In methods (3) and (4), silver salts are used and thus the processing in these methods is complicated and the cost is high. Method (5) is a relatively complete method, but there remains a problem in that silicone dust remaining on the surface of the offset printing plate must be removed.

Recently, there has been remarkable development in the area of lasers. In particular, solid state lasers and semiconductor lasers having a luminous band from near infrared wavelengths to infrared wavelengths and which are small-sized and have a high energy output have become commercially available. These lasers are very useful as exposure light sources for exposure when LDI is required.

Thermally sensitive imaging elements are classified as compositions that undergo chemical transformation(s) in response to exposure to, and absorption of, suitable amounts of heat energy. The nature of thermally induced chemical transformation may be to ablate the composition, or to change the solubility of the composition in a particular developer, or to change tackiness of the surface, or to change the hydrophilicity or the hydrophobicity of the surface of the thermally sensitive layer. As such, selective heat exposure of predetermined areas (imagewise distribution of heat energy) of a film or layer formed of a thermally-sensitive composition has the capability of directly or indirectly producing a suitably imaged pattern of composition which can serve as a resist pattern in printed circuit board fabrication, or in production of lithographic printing plates. Positive working systems based on novolak-diazoquinone resins are an imaging mainstay of the computer chip industry (see, e.g. R. R. Dammel, "Diazonaphthoquinone-based Resists", Tutorial text No. 11, SPIE Press, Bellingham. WA, 993).

Compositions of light sensitive novolak-diazoquinone resins are also widely used in the printing plate fabrication. The light sensitive diazonaphthoquinone derivatives (DNQ) added to novolak resins (a phenol-formaldehyde condensation polymer) slows

down the dissolution of the resin. A revised molecular mechanism of novolak-DNQ imaging materials has been suggested (A. Reiser, Journal of Imaging Science and Technology, Volume 42, Number 1, January/February 1998, pp. 15-22). This text teaches that the basic features of the imaging phenomena in novolak-  
5 diazonaphthoquinone compositions is the observed inhibition of dissolution of the resin, based on the formation of phenolic strings by the interaction of the strong hydrogen acceptor which acts as a solubility inhibitor with the OH groups of the resin. On exposure, the hydrogen bonding between the phenolic strings is severed during a reaction known as the Wolff rearrangement, which follows photolysis of the  
10 diazoquinone moiety of the inhibitor molecule. This rearrangement is not only very fast, but also highly exothermic. ( $\Delta H^\circ$  is at least -66 kcal/mol). The sudden appearance at the location of the solubility inhibitor of a heat pulse of that magnitude, causes a temperature spike of not less than about 220°C. At the high temperature that is produced at the location of the solubility inhibitor, the phenolic  
15 string is severed from its anchor at the DNQ and becomes inactive (dispersed). This happens because it is no longer held together by the inductive effect of the solubility inhibitor.

This model may also explain the fact that a wide range of heat sensitive compositions  
20 based on novolak resins, wherein different types of inhibitors were incorporated, have appeared in patent literature and in commercial announcements. For example, positive-working direct laser addressable printing form precursors based on phenolic resins sensitive to UV, visible and/or infrared radiation have been described. See, for example, U.S. Patent 4,708,925, U.S. Patent 5,372,907 and U.S. Patent 5,491,046.

25 In U.S. Patent 4,708,925, the phenolic resin dissolution in alkaline solution was decreased by a radiation-sensitive onium salt, such as triphenylsulfoniumhexafluorophosphate, instead of DNQ, with the native solubility of the resin being restored upon photolytic decomposition of the onium salt. The onium salt composition is intrinsically  
30 sensitive to UV radiation and can be additionally sensitized to infrared radiation.

U.S. Patents 5,372,907 and 5,491,064 utilize direct positive-working systems based on a radiation-induced decomposition of a latent Bronsted acid to increase the solubility of the resin matrix on imagewise exposure. The described compositions can  
35 be additionally utilized as a negative-working system with additional processing after

imaging and predevelopment. The onium salts, the quinonediazide compounds or the like are not necessarily highly compatible with the alkali aqueous solution soluble polymer compound or the material that absorbs light to generate heat. Thus, it is difficult to prepare a uniform coating solution and to obtain a uniform and stable material for laser direct imaging.

In U.S. Patents 6,037,085 and 5,962,192 thermal laser-sensitive compositions are described based on azide-materials wherein a dye-component is added to obtain the requisite sensitivity.

A wide range of thermally-induced compositions, useful as thermographic recording materials, are disclosed in patent GB 1,245,924, whereby the solubility of any given area of the imageable layer in a given solvent can be increased by the heating of the layer by indirect exposure to a short duration high intensity visible light and/or infrared radiation transmitted or reflected from the background areas of a graphic original located in contact with the recording material. Several systems are described which operate by many different mechanisms and use different developing materials ranging from water to chlorinated organic solvents. Included in the range of aqueous developable compositions disclosed, are those that comprise a novolak type phenolic resin. The patent describes coated films of such resins that show increased solubility on heating. The compositions may contain heat-absorbing compounds such as carbon black or Milori Blue (C.I. Pigment Blue 27); these materials additionally color the images for their use as a recording medium.

Other compositions that include dissolution-inhibiting materials are described in the patent literature. Examples include WO 97/39894, WO 98/42507, WO99/08879, WO99/01795, WO99/21725, US 6,117,623, US 6,124,425, EP 940266 and WO 99/11458. However, the infrared dye, or the like, functions only as a dissolution-inhibiting agent in the non-exposed portions (the image portions), and does not promote the dissolution of the binder resin in the exposed portions (the non-image portions).

Several materials capable of increasing the sensitivity of positive-working compositions have been described. Cyclic anhydrides as sensitizers are described in U.S. Patent 4,115,128; examples include phthalic anhydride, succinic anhydride and

pyromellitic anhydride. Phenols and organic acids have also been described in JP-A Nos. 60-88942 and 2-96755. Specific examples include bisphenol A, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, p-toluenesulfonic acid, dodecylbenzenesulfonic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, terephthalic acid, lauric acid, and ascorbic acid or the like. However, all these materials increase the solubility of the non-exposed portion of the coating, resulting in a reduction in the robustness of the imageable composition to the development process.

Heat-sensitive compositions in which materials are added to enhance the development of the compositions in exposed portions and that do not substantially change the solubility of the unexposed coating are not described by the current state of the art.

## Summary of the Invention

A positive radiation-sensitive composition for use with a radiation source comprises one or more polymers capable of being dissolved in an alkali aqueous solution and a development-enhancing compound. The sensitivity of a radiation-imageable layer formed of the composition of this invention is increased without compromising the handling characteristics. The invention provides a positive-working photosensitive composition for use with a radiation source in lithographic applications, such as conventional imaging systems, computer-to-plate systems or other direct imaging elements and applications. The composition is stable in its state before exposure and has excellent handling properties.

According to a first broad aspect of the invention, there is provided a radiation-sensitive composition comprising at least one aqueous alkali-soluble polymer and a development-enhancing compound. The addition of the development-enhancing compound increases the rate at which the polymer dissolves in an aqueous alkaline developer after illumination with radiation. It is preferred to include a light-to-heat converting compound in the composition to match the sensitivity range of the composition to the wavelength of incident radiation. The development-enhancing compound has a functional group that is at least one of an alcohol, a phenolic hydroxyl, a carboxyl, a carboxylate, a thiol, a thiophenol, a thioacid and its salts, an amine, an imine, an amine oxide, an amide, an imide, a phosphate ester, a

polysiloxane having free hydroxyl groups, an organic or inorganic lithium salt and a fluorine-containing radical.

According to a second broad aspect of the invention, there is provided a positive-working lithographic printing precursor having a coating comprising the composition as aforesaid that is imageable by radiation, preferably infrared radiation, and is developable using an alkaline aqueous developer solution. In a further aspect of the invention, there is provided a positive-working lithographic printing master comprising a precursor as aforesaid, imaged and developed. As further aspects of the invention, there are provided methods for the preparation of the precursor and the master.

The present invention provides novel positive-working imageable compositions and elements and has advantages in that the image forming capability of an imageable layer comprising a polymer compound is improved, places in which the composition can be handled are not restricted, handling of the composition is easy because of the stability of the state before development, and the development latitude is good.

#### **Detailed Description of the Preferred Embodiment**

The inventors have studied positive-working radiation-sensitive compositions, and have found that specific combinations of an alkali aqueous solution soluble polymer compound and certain development-enhancing compounds for increasing the sensitivity of the said composition to the laser radiation does not diminish the development latitude to a large extent.

According to the present invention, a positive radiation-sensitive composition for use with a radiation source comprises, as component (A), one or more polymer compounds capable of being dissolved in an alkali aqueous solution, and a compound (B), referred to herein as a development-enhancing compound.

The polymer component (A) has some degree of solubility in alkaline aqueous solution, though preferably a low degree. In a radiation-sensitive coating formed from the compositions of the invention, the polymer has low solubility due either to its

inherently low solubility, or due to interactions of moieties within its own molecules or interaction with other materials in the composition, for example based on hydrogen bonding or the like.

5 The positive-working radiation-sensitive composition of the present invention may be coated on a suitable hydrophilic lithographic base to form a radiation-sensitive imageable layer. When the imageable layer is illuminated, it becomes more soluble in alkaline aqueous solution. The result is a decrease in the energy needed in exposing the composition to obtain a desired level of developability, as compared with a coating  
10 that does not contain compound (B). Areas of the composition that are not exposed to the radiation (and are therefore not heated by it) do not exhibit significant change in the rate of dissolution in developer. It is to be understood that an increase in the rate of dissolution of the coating means, for purposes of the invention, an increase that is an amount useful in the image-forming process. It does not include any increase that  
15 is less than a useful amount. The invention provides a positive photosensitive composition for use with a radiation source in lithographic applications, such as conventional imaging systems, computer-to-plate systems or other direct imaging elements and applications. It is stable in its state before exposure and has excellent handling properties.

20 It is to be understood that the polymer compounds of component (A) have some, though preferably low, solubility in the alkaline aqueous solution in the non-irradiated (i.e. unheated) areas of the coating, and higher solubility in the irradiated areas, due to the action of the enhancer. It is this differential in solubility that permits  
25 developability of the image that is formed by the radiation.

Without being bound by any theory, the inventors believe the mechanism by which the development-enhancing compounds act in the coating to be by the partial disruption of the hydrogen bonding in the coating by substituting themselves to the  
30 polar groups of the polymer. The partial substitution of these development-enhancers in the system of hydrogen bonding in the polymer, may therefore result in lower imaging energy being required to obtain a desired developability of the coated layer. It is thought that the disruption of hydrogen bonding is due to the small molecules

becoming mobile at a lower temperature than the relatively stiff polymer chains, allowing them to break free from the hydrogen bonding more easily. Damage done to the toughness of the coating by the sudden mobility on-set of the small molecules could therefore be higher than the damage done by the relaxation of hydrogen  
5 bonding in macromolecules. It is thought that the destruction of the hydrogen bonding of the polymer (A) creates a looser solid structure through which the alkaline developer can penetrate more easily, than if compound (B) were absent. The development-enhancing compounds are accordingly thought to be hydrogen bond-substituting compounds.

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One important component of the practice of the invention is the selection of the thermally sensitive polymer component for the positive-acting resist layer. In one preferred embodiment of the present invention, the polymer used as component (A) is a polymer compound having in the molecule any one of a phenolic hydroxide group, a  
15 sulfonamide group, and an active imide. The polymer compound having the phenolic hydroxide group may, for example, be a novolak resin such as phenol formaldehyde resin, m-cresol formaldehyde resin, p-cresol formaldehyde resin, m-/p-mixed cresol formaldehyde resin, phenol/cresol (any one of m-, p-, and mixed m-/p-) mixed formaldehyde resin, or may be pyrogallol acetone resin. The novolak resin having a  
20 phenolic hydroxide group preferably has a weight-average molecular weight of from 500 to 20,000, and a number-average molecular weight of from 200 to 10,000.

As described in U.S. Patent 4,123,279, there may at the same time be used a condensed compound of formaldehyde and phenol resin having, as a substituent, an  
25 alkyl group having 3-8 carbon atoms, such as t-butylphenol formaldehyde resin or octylphenol formaldehyde resin. A single resin having a phenolic hydroxide group may be used alone, or two or more resins having a phenolic hydroxide group may be used together.

30 Phenol-containing polymers obtained by the polymerization of phenol-containing monomers may be used. Specific, preferred examples of such monomers include N-(4-hydroxyphenyl)acrylamide, N-(4-hydroxyphenyl)methacrylamide, o-hydroxyphenylacrylate, m-hydroxyphenylacrylate, p-hydroxyphenylacrylate, o-hydroxyphenylmethacrylate, m-hydroxyphenylmethacrylate, p-



hydroxyphenylmethacrylate, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, and the like.

5 U.S. Patent 6,255,033 Levanon et al. describes an acetal resin having phenolic groups, and formed by the condensation of polyvinyl alcohol with aldehydes. It can be used in the present invention either alone or in combination with other phenolic-containing resins and is suitable for use in the preferred embodiments. This polymer has the advantage that many different functional groups can be incorporated into it to tailor its properties to the specific laser direct imaging application that is needed.

10 Examples of aldehydes that can be used in condensation include, for example, acetaldehyde, n-heptaldehyde, 2,4-dihydroxybenzaldehyde, 2-, 3- or 4-hydroxybenzaldehyde, vanillin, glyoxylic acid and propargyl aldehyde, for example, long chain alkyl aldehydes to reduce the softening point (T<sub>g</sub>) of the polymer for ease of lamination for a dry film photoresist or aromatic aldehydes, such as

15 cinnamaldehyde to increase the oleophilicity of the composition for use in a printing plate. The polymer preferably has a molecular weight range from 3,000 to 100,000.

Other alkali soluble polymers or resins, suitable for use in this invention in a laser direct imaging composition, contain a sulfonamide group or an active imide group as

20 the main functionality. The polymers/resins may be obtained from a low molecular weight compound (monomer or oligomer) having in the molecule one or more sulfonamide groups in which at least one hydrogen atom is bonded to the nitrogen atom, and one or more unsaturated bonds which can be polymerized. Among these, a preferred choice is a low molecular weight compound having a group such as acryl, methacryl, acryloyl, methacryloyl, allyl, allyloxy, vinyl, vinyloxy, vinyl ester, allyl ester

25 and a substituted or mono-substituted aminosulfonyl group or substituted sulfonylimino group. Specifically, there may be preferably used m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide, or the like.

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For a polymer compound having mainly an active imide group, specific examples include N-(p-toluenesulfonyl)methacrylamide or N-(p-toluenesulfonyl)acrylamide.

As the polymer compound (A) in the present embodiment, there may be used not only a polymer compound having, as the main structural unit, any of the functional groups previously mentioned, and mixtures of such compounds, but also a resin containing,  
5 as a copolymerized component, 10 mole % or more of at least one functional group selected from phenolic, sulphonamide or active imino. The copolymer may also contain copolymerized components other than phenolic, sulphonamide or active imino.

10 Examples of other copolymerized components which may be used are the following monomers:

Acrylic esters and methacrylic esters having an aliphatic hydroxyl group such as 2-hydroxyethylacrylate or 2-hydroxyethylmethacrylate, alkyl (meth)acrylates such as  
15 methyl acrylate, hexyl acrylate, benzyl acrylate, glycidyl acrylate, methyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, glycidyl methacrylate, and N-dimethylaminoethyl methacrylate, (meth)acrylamides such as acrylamide, methacrylamide, N-methylolacrylamide, N-hexylmethacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, vinyl ethers such as ethylvinyl ether, 2-  
20 chloroethylvinyl ether, hydroxyethylvinyl ether, and phenylvinyl ether, vinyl esters such as vinyl acetate, vinyl chloroacetate, styrenes such as styrene, .alpha.-methylstyrene, and chloromethylstyrene, vinyl ketones such as methylvinyl ketone and phenylvinyl ketone, olefins such as propylene, isobutylene, butadiene, and isoprene, N-vinylpyrrolidone, N-vinylcarbazole, acrylonitrile, unsaturated imides such  
25 as maleimide, N-acryloylacrylamide, and unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic anhydride, and itaconic acid.

The polymer compounds described in this specification, whether it is a homopolymer or a copolymer, preferably has a weight-average molecular weight of 2,000 to  
30 300,000, and a dispersion degree (weight-average molecular weight/number-average molecular weight) of from 1.1 to 10.

Polymer compound (A) may be used alone, or two or more types may be used in combination. The amount thereof is from 30 to 99 weight %, preferably from 40 to 95

weight %, and especially preferably from 50 to 90 weight % of the entire content of solids in the printing plate material. If the added amount of the polymer compound is less than 30 weight %, the durability of the imageable layer deteriorates. If the added amount is more than 99% by weight, both the sensitivity and durability deteriorate.

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The development-enhancing compound (B) of the invention contains functional groups that can substitute themselves in the system of hydrogen bonding existing in the polymer, thereby enhancing the ability of polymer to de-structure under the action of radiation. These functional groups are preferably polar groups comprising one or more of the following types: alcohols (preferably polyol), phenolic hydroxyl (preferably but not limited to di- or tri-hydric phenols), carboxyl, carboxylate (preferably but not limited to lithium carboxylate), thiol, thiophenol, thioacid and salts, amine, amine oxide, imine, amide, imide, quaternary ammonium salts, fluorine-containing compounds, phosphate-containing esters and amides, phosphorous-containing quaternary ammonium compounds, and polysiloxane with free hydroxyl groups.

It is desired, but not necessary, for the above development-enhancing compounds to have also a hydrophobic segment (radical) in the molecule. Without wishing to be limited by any proposed mechanism, the inventors believe the hydrophobic segment of the molecule either remains in the coating, or it places itself at the interface with air. In both cases, it is considered possible that the hydrophobic segment reduces the rate of alkali diffusion in the coating thereby protecting it against excessive weight loss in developer. Because of this dual hydrophilic/hydrophobic or amphiphilic structure, many of the candidate development-enhancing compounds are surfactants.

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Preferred development-enhancing compounds are of the following types:

1. Hydroxyl- and thiol-containing compounds such as alcohols (preferably polyols), phenols, thiols and thiophenols. The alcohols may have an alkyl radical of  $C_{12}-C_{60}$  or a  $C_4-C_{60}$  fluoroalkyl or a  $C_7-C_{60}$  fluoroalkylaryl. The polyols may be  $C_3-C_{500}$ . Examples are propanetriol, butanetetrole, sorbitol and sorbitol esters (called sorbitanes). Phenols are preferably polyhydric. Examples of dihydric phenols are resorcinol and alkyl resorcinols such as 4-hexylresorcinol and n-dodecylresorcinol, and catechol and alkyl catechols. Examples of trihydric

phenols are: pyrogallol, phloroglucinol, 1,2,4-benzenetriol and their alkyl or fluoroalkyl derivatives.

2. Lithium salts of organic acids such as lithium carboxylates, thiocarboxylates, sulphates, sulfonates, phosphates, phosphites, nitrates and nitrites. Examples of lithium salts of organic acids are lithium 3-(1H,1H,2H,2H-fluoroalkyl) propionate and 3-[(1H,1H,2H,2H-fluoroalkyl)thio]propionate, lithium trifluoromethane sulfonate and lithium perfluorooctylethylsulfonate.
3. Compounds containing at least one of the amine, amine oxide, imine, amide, imide functional groups, and preferably containing two such groups and having a molecular weight of 500-20,000 daltons.
4. Esters, amides and quaternary ammonium salts of phosphorous-containing acids, preferably having free hydroxyl groups. Examples of phosphorous-containing esters are those with structures  $P(OH)(OR)_2$ ,  $P(OH)_2(OR)$ ,  $P(OH)_2[O-R-N(CH_2-CH_2-OH)_2]$ ,  $P(OR)_2[O-R-NH(CH_2-CH_2-OH)_2]$ , where R is an alkyl, aryl, alkylaryl, polyethylene oxide, polypropyleneoxide or combination thereof, and where the R radical may contain fluorine atoms. Other suitable compounds are alkyl phosphonic acids,  $R-P(O)(OH)_2$ , as well as their esters and salts, where R is as defined above. Examples of suitable phosphorous-containing amides are  $P(OH)(ONHR)_2$ ,  $P(OH)_2(ONHR)$ ,  $P(OR)_2[O-NH(CH_2-CH_2-OH)_2]$ ,  $P(OR)[O-NH(CH_2-CH_2-OH)_2]_2$ , where R is an alkyl, aryl, polyethylene oxide, polypropyleneoxide and combinations thereof, and where R may contain fluorine atoms. An example of a quaternary ammonium salt containing hydroxyl groups is the diethanolamine salt of perfluoroalkyl substituted polyethyleneoxide phosphite.
5. Polysiloxane with free hydroxyl groups. Preferably, the free hydroxyl groups are terminal ones. Examples of suitable compounds are those with structure  $R[OSi(OCH_3)_2]_n-Si(OCH_3)(OH)_2$ , where R is an alkyl, aryl, polyethyleneoxide, polypropyleneoxide group or combinations thereof and n is 2 to 1000.

To provide heat-absorption of the laser energy in the composition of the present invention, a converter substance, capable of absorbing incident infrared radiation and converting it to heat, is preferably incorporated in the coating composition. The radiation absorbing materials suitable for the invented heat-sensitive compositions may be chosen from a wide range of organic and inorganic pigments such as carbon blacks, phthalocyanines or metal oxides. Green pigments: Heliogen Green D8730, D 9360, and Fanal Green D 8330 produced by BASF; Predisol 64H-CAB678 produced

by Sun Chemicals, and black pigments: Predisol CAB2604, Predisol N1203, Predisol Black CB-C9558 produced by Sun Chemicals Corp., are examples of effective heat absorbing pigments, and other classes of materials absorbing in the near infrared region are known to those skilled in the art. The infrared absorbing materials are also the preferable heat absorbing agents for use in the compositions of the invention, especially those absorbing at wavelengths longer than 700 nm, such as between about 700 and 1300, with near infrared absorbing materials (between about 700 and 1000 nm) being generally used.

These pigments may be used with or without being subjected to surface treatment. Methods for surface treatment include methods of applying a surface coat of resin or wax, methods of applying surfactant, and methods of bonding a reactive material (for example, a silane coupling agent, an epoxy compound, polyisocyanate, or the like) to the surface of the pigment. These methods for surface treatment are described in "Properties and Application of Metallic Soap" (published by Saiwai Shobo), "Printing Ink Technology" (CMC Publications, published in 1984) and "Latest Pigment Applied Technology" (CMC Publications, published in 1986).

The particle size of the pigments is preferably from 0.01 to 10  $\mu\text{m}$ , more preferably from 0.05 to 1  $\mu\text{m}$  and especially preferably from 0.1 to 1  $\mu\text{m}$ . A particle size of the pigment of less than 0.01  $\mu\text{m}$  is not preferred from the standpoint of the stability of the dispersed pigment in a photosensitive layer coating liquid. A particle size of more than 10  $\mu\text{m}$  is not preferred from the standpoint of uniformity of the formed infrared sensitive layer.

The method for dispersing the pigment in the composition that can be used may be any known dispersion method that is used for the production of ink or toner or the like. Dispersing machines include an ultrasonic disperser, a sand mill, an attritor, a pearl mill, a super mill, a ball mill, an impeller, a disperser, a KD mill, a colloid mill, a dynatron, a three-roll mill and a press kneader. Details thereof are described in "Latest Pigment Applied Technology" (CMC Publications, published in 1986).

For infrared laser sensitive compositions, the dyes that can be used may be any known dyes, such as commercially available dyes or dyes described in, for example, "Dye Handbook" (edited by the Organic Synthetic Chemistry Association, published in 1970). Specific examples of dyes which absorb infrared or near infrared rays are, for example, cyanine dyes disclosed in Japanese Patent Application Laid-Open (JP-A) Nos. 58-125246, 59-84356, 59-202829, and 60-78787; methine dyes disclosed in JP-A Nos. 58-173696, 58-181690, and 58-194595; naphthoquinone dyes disclosed in JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940 and 60-63744; squarylium colorant disclosed in JP-A No. 58-112792; substituted arylbenzo(thio)pyrylium salts described in U.S. Patent 3,881,924; trimethinethia pyrylium salts described in JP-A No. 57-142645 (U.S. Patent 4,327,169); pyrylium-based compounds described in JP-A Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063, and 59-146061; cyanine colorant described in JP-A No. 59-216146; pentamethinethiopyrylium salts described in U.S. Patent 4,283,475; and pyrylium compounds, Epolight III-178, Epolight III-130 and Epolight III-125 described in Japanese Patent Application Publication (JP-B) Nos. 5-13514 and 5-19702 and cyanine dyes disclosed in British Patent No. 434,875.

The pigments or dyes may be added into the radiation sensitive medium for a printing plate, or to other compositions, such as an etch resist in an amount of from 0.01 to 30 weight %, preferably from 0.1 to 10 weight %, and especially preferably from 0.5 to 10 weight % in the case of the dye and from 3 to 13 weight % in the case of a pigment, with respect to the entire amount of solids in the material for the printing plate. If the pigment or dye content is less than 0.01 weight %, sensitivity is lowered. If this content is more than 30 weight %, uniformity of the photosensitive layer is lost and durability or other properties such as etch resistance of the imageable layer deteriorates.

In a further embodiment of the present invention, the positive radiation-sensitive medium of the present invention is prepared without the converter substance. The radiation-sensitive medium may be incorporated into a positive-working lithographic

printing precursor in an imageable layer that is separate from, but adjacent to, the layer comprising the converter substance. While it is possible to coat the layer comprising the converter substance on top of the imageable layer comprising the radiation-imageable medium, the preferred arrangement is to have the layer  
5 comprising the converter substance sandwiched between the imageable layer and the hydrophilic lithographic base, the imageable layer being transparent to the radiation employed for imaging. When the combined layer structure is illuminated, the layer comprising the converter substance produces heat in the illuminated areas, the heat being then imagewise transferred to the adjacent imageable layer comprising the  
10 radiation-sensitive medium. The radiation-sensitive medium then becomes more soluble in alkaline aqueous solution in the imagewise heated areas. The result is a decrease in the energy needed in exposing the composition to obtain a desired level of developability, as compared with a coating that does not contain compound (B). The term "hydrophilic lithographic base" is used herein to describe a plate or sheet of  
15 material of which at least one surface is hydrophilic, thereby allowing it to hold water or aqueous media, such as fountain solution.

It is possible to have, in place of a separate polymer(A) and infrared absorbing compound, a polymer in which the infrared absorbing material is bonded to the  
20 polymer. Examples of these materials are given in U.S. Patent 6,124,425.

A compound that reduces the solubility of the polymer in the alkaline aqueous solution, herein referred to as a "dissolution inhibitor" may optionally be included in the coating composition. Such compounds include, but are not limited to, dyes,  
25 particularly infrared dyes such as ADS 830A dye (American Dye Source, Montreal, Canada), and certain image colorants, such as Victoria Pure Blue BO (Basic Blue 7, CAS# 2390-60-5). The tetrafluoroborate salt of Basic Blue 7 is preferred. The use of such compounds is preferred where the inherent solubility of the polymer is relatively high.

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In order to achieve stability in processing in a broader range of processing conditions, a surfactant may optionally be included in the compositions of the invention. Suitable nonionic surfactants are described in JP-A Nos. 62-251740 and 3-208514 and amphoteric surfactants described in JP-A Nos. 59-121044 and 4-13149. The amount  
5 of the nonionic or amphoteric surfactant is preferably from 0.05 to 10 weight percent and more preferably from 0.1 to 5 by weight % of the material for the composition.

A surfactant for improving the applying property, for example, any of the fluorine-containing surfactants such as, for example, Zonyl's (DuPont) or FC-430 or FC-431  
10 (Minnesota Mining and Manufacturing Co.) or alternatively polysiloxanes such as Byk 333 (Byk Chemie), may be added into the infrared sensitive layer. The amount of the surfactant added is preferably from 0.01 to 1 weight % and more preferably from 0.05 to 0.5 weight % of the entire material for the composition.

15 Image colorants may optionally be included in the compositions of the invention in order to provide a visual image on the exposed plate prior to inking. As the image colorant, dyes other than the aforementioned salt-forming organic dyes may be used. Examples of preferred dyes, including the salt forming organic dyes, are oil-soluble dyes and basic dyes. Specific examples are Oil-Yellow #101, Oil Yellow #103, Oil  
20 Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS, Oil Black T-505(all of which are manufactured by Orient Chemical Industries Co., Ltd.), Victoria Pure Blue BO, the tetrafluoroborate salt of Basic Blue 7, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000), Methylene Blue (CI52015), or the like. The dyes  
25 described in JP-A No. 62-293247 are especially preferred. The dye may be added into the material for the printing plate in an amount of preferably from 0.01 to 10 weight % and more preferably from 0.5 to 8 weight % of the entire solid contents of the material for the composition.

30 A plasticizer for providing the formed film with softness may be added as needed in the material for the compositions of the invention. The plasticizer may be e.g. butylphthalyl, polyethyleneglycol, tributyl citrate, dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, tetrahydrofurfuryl oleate, an oligomer or



polymer of acrylic acid or methacrylic acid, or the like, sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, monoglyceride stearate, polyoxyethylene-nonylphenylether, alkyldi(aminoethyl)glycine, alkylpolyaminoethylglycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethylimidazolium betaine, N-tetradecyl-N,N-betaine (e.g., trade name Amogen, manufactured by Dai-ichi Kogyo Co., Ltd.), and the like.

Other polymers may be added to reduce the cost of the formulation. Examples include urethane and ketone resins. The amounts of these materials can vary between 0.5% and 25%, preferably between 2% and 20% by weight of solids.

Suitable adhesion promoters may optionally be included in the compositions of the invention. Suitable ones include di-acids, triazoles, thiazoles and alkyne containing materials. The adhesion promoters are used in amounts between 0.01 and 3% by weight.

In general, the composition ratio of the component (A) to the component (B) is preferably from 99/1 to 75/25. The sensitizing compound must be present in an amount that is effective to significantly increase the sensitivity of the coating to the developer in the radiation-exposed areas of the coating, that is, increased by an amount useful in the image-forming process. If the amount of component (B) is lower than this lowest limit, the component (B) does not significantly improve the sensitivity of the coating. If the amount of component (B) is more than the aforementioned upper limit, the tolerance to the developer is significantly reduced. Thus, both cases are not preferred. More preferred ranges for component (B) are 1.5% to 10% and 5% to 7%, measured by weight relative to the total solids in the coating composition.

The positive-working lithographic printing precursor of the present invention can be produced by dissolving the aforementioned respective components into an appropriate solvent, filtering if necessary, and applied from a liquid in a manner

known, such as, for example, bar coater coating, spin coating, rotating coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, and roll coating, or the like, onto a hydrophilic lithographic base. Appropriate solvents include methylenechloride, ethylenedichloride, cyclohexanone, methylethyl ketone, acetone, methanol, propanol, ethyleneglycolmonomethylether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, and toluene or the like. A single solvent may be used alone, or a combination of two or more solvents may be used. The concentration of the aforementioned components (all of the solid components including the additives) in the solvent is preferably from 1 to 50 weight %. The applied amount (of the solid) on the hydrophilic lithographic base obtained after application and drying differs in accordance with the use, but in general, is preferably from 0.3 to 12.0 grams per square meter according to the application. Lesser amounts can be applied to the hydrophilic lithographic base, resulting in a higher apparent sensitivity, but the film characteristics of the material are deteriorated.

The radiation-sensitive compositions of the present invention are useful for production of printing circuit boards, for lithographic printing plates and other heat-sensitive elements suitable for direct imaging, including but not limited to laser direct imaging (LDI). In the case of lithographic printing, the positive-working lithographic printing precursor of the present invention employs a hydrophilic lithographic base which may, in a general case, comprise a separate hydrophilic layer over a substrate, such that, when the precursor is developed, the hydrophilic coating layer remains, and is employed in the printing process for retaining aqueous media such as fountain solution. In such a case, there is great latitude in choosing a substrate on which to coat the hydrophilic layer. Alternatively, the hydrophilic lithographic base may be of a single material and this material, which may typically be aluminum, may be treated to assure a hydrophilic surface property.

Suitable substrates may include, for example, paper; paper on which plastic such as polyethylene, polypropylene, polystyrene or the like is laminated; a metal plate such as an aluminum, anodized aluminum, zinc or copper plate; a copper foil, reverse

treated copper foil, drum side treated copper foil and double treated copper foil clad on a plastic laminate, a plastic film formed of, for example, cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, or polyvinyl acetal; a paper or a plastic film on which the aforementioned metal is vapor-deposited or laminated; glass or glass in which a metal or metal oxide is vapor deposited or the like.

As the substrate in the present embodiment for a printing plate, a polyester film, or an aluminum plate is preferred, and an aluminum plate is especially preferred because of its stable dimensions and relatively low cost. A plastic film on which aluminum is laminated or vapor-deposited may be used. The composition of the aluminum plate applied to the present invention is not specified, and the aluminum plate may be prepared according to any of the known methods, for example of roughening, anodizing and post anodizing treatments. The thickness of the aluminum plate used in the present embodiment is from about 0.1 to 0.6 mm, preferably from 0.15 to 0.5 mm.

The positive-working lithographic printing precursor produced as described above is usually subjected to image-exposure and developing processes. In a preferred embodiment, radiation-sensitive compositions as described above are applied as a coating on a hydrophilic lithographic base (for example an aluminum plate) to form a lithographic printing precursor. The precursor can be imaged (for example by imagewise exposure to infrared radiation), and the imaged precursor developed to a positive-working lithographic printing plate, using a conventional alkaline aqueous developer solution. When the precursor has a separate imageable layer and layer comprising the converter substance, the development process removes both layers, to reveal the underlying hydrophilic surface.

In a preferred embodiment of the invention, the light source for an active light beam which is used in the image-exposure, is preferably a light source emitting light having a luminous wavelength within the range from the near infrared wavelength region to the infrared wavelength region, and is especially preferably a solid state laser or a

semiconductor laser. Preferably, the positive-working lithographic printing precursor based on the radiation-sensitive medium of the present invention is sensitive to radiation of wavelength between 700nm and 1300nm, and more preferably between 700nm and 1000. In a more general embodiment of the present invention, there is no limitation on the wavelength or nature of the radiation source and suitable radiation absorbing agents may be chosen to match the wavelength of the radiation source.

The developing solution and replenishing solution for the positive-working lithographic printing precursor of the present invention may be a conventionally known alkali aqueous solution such as, for example, sodium metasilicate, potassium tertiary phosphate, ammonium secondary phosphate, sodium carbonate, potassium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide, tetraalkylammonium hydroxides; and organic alkali agents such as, alkyl amines, alkyl ethanolamines or diamines. The alkali agent may be used alone, or a combination of two or more may be used.

Among these, especially preferred developing solutions are aqueous solutions of silicates and hydroxides. It is known that when development is carried out by using an automatic developing machine, an aqueous solution (a replenishing solution) having a higher basicity than that of the developing solution is added to the developing solution so that many plates or pieces of can be processed without having to replace the developing solution in the developing tank for a long time. In the present embodiment, such a replenishing manner is preferably used. Various surfactants or organic solvents may be optionally added to the developing solution and the replenishing solution to accelerate or control developability, improve the dispersibility of development-scum, and/or improve the affinity of image portions on the printing plate with ink. Other agents commonly used in positive plate developers may also be included in the developer solution.

The composition is usually post-processed with water; optionally containing, for example, a surfactant. In the case of printing plates a desensitizing solution containing gum arabic or a starch derivative is used. Various combinations of these

treatments can be used as the post-processing carried out when the imageable medium of the present embodiment is used in its different applications.

### **EXAMPLES**

- 5 The following examples illustrate aspects of the invention. Materials were obtained from the following sources:

Mowiol 3-83 (trademark), a polyvinyl alcohol product from Hoechst, Germany.

- 10 Tween 80K (trademark) from Avecia of Manchester, UK.

ADS 830A and ADS 830WS (trademarks) IR dyes from American Dye Source, Montreal, QC, Canada.

- 15 Phosphate esters Zelec 8172 and 8175 (trademarks) from Stepan UK Ltd, Cheshire, UK .

Zonyl FSA (trademark) from DuPont Canada Inc., Mississauga, ON, Canada.

- 20 Silicone acrylate VS-80 (trademark) from 3M, St. Paul, MN, USA.

Dimethicone copolyol SF1488 (trademark) from GE Silicones, Waterford, NY, USA.

- 25 Goldstar Plus (trademark) positive plate developer from Kodak Polychrome, Mississauga, ON, Canada.

#### **Preparation of Polymer 1:**

- 30 110 grams of Mowiol 3-83 polyvinyl alcohol (an 83% hydrolyzed polyvinyl acetate having a number average molecular weight of about 14,000), was added to a closed reaction vessel fitted with a water-cooled condenser, a dropping funnel and thermometer, containing 110 grams of demineralized water and 110 grams of methanol. With continual stirring, the mixture was heated for 0.5 hour at 80°C until

became a clear solution. After this, the temperature was adjusted to 60°C and 3 grams of concentrated sulfuric acid in 100 grams of propyleneglycol monomethylether (PM) was added. Over a 15 minutes period, a solution of 65 grams of 3-hydroxybenzaldehyde and 1.4 grams of 2,6-di-t-butyl-4-methylphenol in 450 grams of PM was added in a drop-wise manner. The reaction mixture was diluted with additional 200 grams of PM, and 9.2 grams of n-butyraldehyde in 200 grams of PM was added in a dropwise manner, upon complete addition of the aldehydes, the reaction was continued at 50°C for additional 3 hours. At this stage the conversion of the butyraldehyde is completed and the conversion of the 3-hydroxybenzaldehyde is close to 50%. 500 grams of trimethyl orthoformate was added to the reaction mixture in a dropwise manner under stirring. After addition of the trimethyl orthoformate the conversion of 3-hydroxybenzaldehyde reached 100% (less than 0.1% of water in the reaction mixture). The resultant polymer is referred to as Polymer 1 in subsequent examples. The reaction mixture is precipitated in water. The resulting polymer is filtered, washed with water and dried at 60° C for 3 days to a water content of 0.2%.

#### **Preparation of Polymer 2:**

The preparation of polymer 2 is identical to that of polymer 1 except that 58.5 g of 3-hydroxybenzaldehyde in 400 g of PM is added first, followed by 7 g of cinnamaldehyde in 50 g of PM and followed by 9.2 g of butyraldehyde in 200 g of PM. The presence of cinnamaldehyde in the composition of polymer 2 is thought to improve the ink-attracting ability of the imageable areas of the plate.

#### **Comparative Example 1:.**

This is a reference example containing no development-enhancing compound.

A coating solution was made of the following additives (wt%):

- polymer 1:polymer 2, 45:55, 77.5%;
- a cyanine dye with the formula  $C_{47}H_{47}ClN_2O_3S$ , CAS#134127-48-3, 1% as an infrared absorber;
- an image colorant Victoria Pure Blue BO (Basic Blue 7, CAS# 2390-60-5) in the amount of 6.5%;
- a polyethylene glycol sorbitan ester, Tween- 80, with a degree of polymerization 80 as 5%.

The coating solution was made in acetone: methoxypropanol (Dowanol PM), 75:25 and had a percentage of solids of 10%. A printing plate was cast manually on anodized aluminum substrate with a casting rod #12 (coating weight 1.75-1.8 g/m<sup>2</sup>). The plate was dried at 130 °C in a traveling oven (Wisconsin model SPC MINI-  
5 34/121) for 3 min to remove the solvent to a residual level of 1.5%.

The plate was then imaged using a Creo Quantum 800 (trademark) imagesetter with 12 W radiation, wavelength 830 nm and an energy density series between 180-400 mJ/cm<sup>2</sup> in increments of 20 mJ/cm<sup>2</sup> under the form of solid image squares. The plate  
10 was developed in a Glunz-Jensen 85 HD processor in an alkaline developer containing 7% sodium metasilicate of conductivity 66 mS/cm. The developing conditions were: 24°C, 30s passing time, and 50°C drying. The developed plate revealed squares of bare substrate where the optical density was measured with an optical densitometer. The clearing point was defined as the energy at which the  
15 optical density (OD) difference between the area of cleared substrate and the original uncoated substrate was 0.01 or less. The plate prepared under this example had a clearing point of 350 mJ/cm<sup>2</sup> and a weight loss in developer of 20%. The weight loss in developer refers to the non-irradiated area.

## 20 **Example 2:**

This example demonstrates the use of a lithium compound, lithium trifluoromethane sulfonate as a development enhancing compound.

The following coating composition was prepared:

- 25
- polymer 1:polymer 2, 45:55, 84.5%, both prepared as per example 1
  - infrared dye 1%
  - Basic Blue 7, 6.5%
  - Tween-80, 5%
  - lithium trifluoromethane sulfonate, 3%

30

A coating solution containing 10% solids was prepared with the above formula. Plates were cast manually on anodized aluminum with the solution in Example 1 (reference) and in the above solution. The plates were dried at 125 °C for 3 min. A coating weight of 1.8 g/m<sup>2</sup> was obtained. The plate was imaged in a Creo Quantum 800 imagesetter  
35 with 12 W radiation and a wavelength of 830 nm. The image was a series of solid

squares irradiated with an energy density between 120-360 mJ/cm<sup>2</sup> in increments of 20 mJ/cm<sup>2</sup>. The plates were developed in a developer containing 7% sodium metasilicate (conductivity 66 mS/cm) at 23 °C, using a residence time in the processor of 30 s. The plate with lithium trifluoromethane sulfonate development-enhancer had a clearing point of 140 mJ/cm<sup>2</sup> and a weight loss in developer of 28% as compared with the reference without development-enhancer, which had a clearing point of 320 mJ/cm<sup>2</sup> and a weight loss of 20%.

### **Example 3:**

- 10 This example employs nonylphenol phosphate ester (Zelec 8175) as a development-enhancing compound. The performance of the plate containing Zelec 8175 is compared with that of the reference plate in Example 1.

A coating was made with the composition:

- 15 - polymer 1:polymer 2,1:1, 77.5%  
- Basic Blue 7, 6.5%  
- IR dye 1%  
- Tween-80 5%  
- Zelec 8175, 10%

20

- The coating solution was made at 10% solids in acetone: Dowanol PM, 75:25. A plate with a coating weight of 1.65-1.75 g/m<sup>2</sup> was cast with this solution. A reference plate with the reference solution in Example 1 was cast at the same time. The two plates were dried at 125°C for 2 min. The plates were imaged in Creo's Quantum 800  
25 imagesetter with 12 W radiation of wavelength 830 nm and an energy density series between 120-360 mJ/cm<sup>2</sup> in increments of 20 mJ/cm<sup>2</sup>. The plates were developed in Goldstar positive plate developer diluted to 90% of its original concentration, at 23 °C, for 30s. The plate with Zelec 8175 development-enhancer had a clearing point of 110 mJ/cm<sup>2</sup> and a weight loss in developer of 25% as compared with the reference plate  
30 without development-enhancer that had 320 mJ/cm<sup>2</sup> clearing point and a weight loss of 18%.

### **Example 4:**

- This example employs Zelec 8172 phosphate ester as a development-enhancing  
35 compound and compares it with the reference coating in Example 1.



A coating was made with the composition:

- polymer 1:polymer 2,1:1, 77.5%
- Basic Blue 7, 6.5%
- 5 - IR dye 1%
- Tween-80 5%
- Zelec 8172, 10%

Two plates were cast manually, one with the above solution containing Zelec 8172 as  
10 a development-enhancer and one with the reference solution in Example 1 without  
development-enhancer. The plates had a coating weight of 1.7-1.8 g/m<sup>2</sup>. The plates  
were dried at 125°C, 2min and imaged with 12 w an energy series between 80-  
300mJ/cm<sup>2</sup>. The plates were developed in 60% Goldstar at 23°C, 30 s. The clearing  
point and weight loss in developer were 140 mJ/cm<sup>2</sup> and 35%, respectively for the  
15 plate containing Zelec 8172 while the reference plate without development-enhancer  
did not clear up to 300 mJ/cm<sup>2</sup>.

#### **Example 5:**

This example shows the use of an anionic surfactant based on lithium thiocarboxylate  
20 as a development-enhancing compound.

A coating was made containing the following additives:

- Polymer 1:Polymer 2, 1:1, 86%.
- IR dye 1%
- 25 - Basic Blue 7, 6.5%
- Tween-80, 5%
- Lithium 3-[(1H,1H,2H,2H-fluoroalkyl)thio]propionate (Zonyl FSA from DuPont), 1.5%

A coating with the above formula and a reference coating as in Example 1 containing  
30 the same ingredients except Zonyl FSA were prepared. The coating solutions were  
made in Dowanol PM at 10% solids. Plates were cast manually on anodized  
aluminum substrate and baked at 125°C, for 2.5 min. The coating weight was  
determined as 1.7-1.8 g.m<sup>2</sup>. The plates were imaged in identical conditions: power 11  
w and an energy density series of 100-350 mJ/cm<sup>2</sup>. The plates were developed in a  
35 developer containing 7.2% sodium metasilicate (conductivity 66 mS) at 24°C and 30s

residence time in developer. The reference plate containing no enhancer had a clearing point of 320 mJ/cm<sup>2</sup> and a weight loss in developer of 15%, while the plate containing 1.5% FSA had a clearing point of 130 mJ/cm<sup>2</sup> and a weight loss in developer of 25%.

5

**Example 6:**

This example shows the use of a compound containing phenolic hydroxyls, n-dodecyl resorcinol as a development-enhancing compound.

- 10 A plate was made with a coating containing 7% n-dodecyl resorcinol and compared with a reference plate.

The coating in this example had the following composition:

- Polymer 1:polymer 2,1:1, 80.5%
  - 15 - Basic Blue 7, 6.5%
  - IR dye 1%
  - Tween-80, 5%
  - n-Dodecyl resorcinol, 7%
- 20 The coating solution in this example and the reference coating (as in Example 1) were made in acetone: Dowanol PM, 75:25 at 10% solids. The solutions were cast with a rod on anodized aluminum substrate. The resulting plates were baked at 130°C for 3 min to a residual solvent level of 1.5%. The coating weight was 1.7 g/m<sup>2</sup>. The plates were exposed to a 830 nm IR laser radiation at a power of 8W and an energy density series of 90-400 mJ/cm<sup>2</sup>. The plates were developed in a DuPont-Howson processor in a developer containing 7% sodium metasilicate of conductivity 71 mS/cm in the following conditions: 23°C and 30 s residence time. The plate with n-dodecyl resorcinol showed a clearing point of 160 mJ/cm<sup>2</sup> and a weight loss in developer of 28% as compared to the reference plate which showed 350 mJ/cm<sup>2</sup> clearing point and a weight loss of 15%.
- 25
- 30

**Example 7:**

- 35 This example shows the use of an organic polysiloxane (the silicone acrylate VS-80 from 3M) ending in two free hydroxyl groups as a development-enhancing compound.

The composition of the coating with the silicone compound is the following:

- Polymer 1:polymer 2,1:1, 82.5%
- Basic Blue 7, 6.5%
- 5 - IR dye 1%
- Tween-80, 5%
- Silicone acrylate VS-80, 5%

- 10 A reference coating without development-enhancer as in Example 1 was used for comparison. The solutions were made in acetone: Dowanol PM, 75:25 at 10% solids. Plates were cast manually and were baked at 130°C/3min. The coating weight was 1.8-1.85 g/m<sup>2</sup>. The plates were imaged with 12 W and an energy series of 90-350 mJ/cm<sup>2</sup>. The plates were developed in Goldstar (Kodak) positive plate developer in a DuPont-Howson processor in the following conditions: 23°C and 30s passing time.
- 15 The plate with silicone acrylate development-enhancer had a clearing point of 150mJ/cm<sup>2</sup> and a weight loss in developer of 27% as compared to 300 mJ/cm<sup>2</sup> and 15% weight loss for the reference.

## 20 **Example 8**

- A. This example demonstrates the use of a phenolic compound having two hydroxyl groups as a development enhancer.

- 25 A coating composition with the following composition was prepared:

- Polymer 1:polymer 2,1:1, 77.5%
- Tetrafluoroborate salt of Basic Blue 7, 6.5%
- IR dye 1%
- Tween-80, 5%
- 30 - Resorcinol, 10%

A reference coating without development enhancer as in Example 1 was used for comparison. The coating solutions were made in acetone: Dowanol PM, 75:25 at 10% solids. For this Example, a dye was prepared and used that is

based on the triarylmethane dye Basic Blue 7 (CAS number 371231-05-9). Specifically the tetrafluoroborate ( $\text{BF}_4^-$ ) salt of Basic Blue 7 was used. Plates were cast manually with a casting rod and were dried at  $130^\circ\text{C}/3\text{min}$ . The coating weight was  $1.8\text{--}1.85\text{ g/m}^2$ . The plates were imaged with 12 W and an energy series of  $90\text{--}350\text{ mJ/cm}^2$ . The plates were developed in a developer containing 7% sodium metasilicate (conductivity 66 mS/cm) in a DuPont-Howson processor in the following conditions:  $26^\circ\text{C}$  and 30s passing time. The plate with resorcinol development enhancer had a clearing point of  $150\text{mJ/cm}^2$  and a weight loss in developer of 26% as compared to  $350\text{ mJ/cm}^2$  and 15% weight loss for the reference plate.

B. A further composition was prepared using resorcinol as the development-enhancing compound. A polyvinyl alcohol polymer was used that was produced from the reaction of polyvinyl alcohol with butyraldehyde and 2-hydroxybenzaldehyde:

- Polyvinyl acetal polymer 55.46%
- Phenolic polymer, Bakelite 9900 19.45%
- Resorcinol 19.45%
- IR dye (830 nm) 0.97%
- IR dye (775 nm) 0.78%
- Victoria Blue R dye 2.43%
- Sudan Black B stabilizer 0.97%
- NN Diethylaniline 0.49%

A coating solution containing 10% solids in solvent (MEK 78%, Dowanol PM 22%) was prepared using the above formula. It was used as described in Example 8A, with comparable results.

#### **Example 9:**

This example demonstrates the use of a phenolic compound having two hydroxyl groups that has the ability of interfering with the system of hydrogen bonding in the polymer and acts as a development-enhancer. The compound is 4-hexyl resorcinol.

A plate was made with a coating containing 5% 4-hexyl resorcinol having the composition in Table 1. A reference coating with no development-enhancer having

the composition in Table 1 was also prepared. The coating solutions were made in acetone: Dowanol PM, 75:25 at 10% solids. The solutions were cast with a rod on anodized aluminum substrate. The resulting plates were baked at 130°C for 3 min to a residual solvent level of 2%. The plates were exposed to 830 nm IR laser radiation a power of 8W and an energy density series of 90-350 mJ/cm<sup>2</sup>. The plates were developed in a DuPont-Howson processor in a developer containing 7% sodium metasilicate of conductivity 71 mS/cm in the following conditions: 23°C and 30 s residence time. The plate with 4-hexyl resorcinol showed a clearing point of 150 mJ/cm<sup>2</sup> as compared to the reference plate with no development-enhancer that cleared up at 320 mJ/cm<sup>2</sup>. The weight loss in developer of the two plates was 27% and 17%, respectively.

Table 1

|                                    | Reference | Example 9 |
|------------------------------------|-----------|-----------|
| Polymer1:Polymer 2, 54:46          | 87.5      | 82.5      |
| IR dye                             | 1         | 1         |
| Basic Blue 7                       | 6.5       | 6.5       |
| Tween-80                           | 5         | 5         |
| 4-hexyl resorcinol                 | -         | 5         |
| Clearing point, mJ/cm <sup>2</sup> | 320       | 150       |
| Weight loss in developer, %        | 17        | 27        |

#### Example 10:

This example shows the use of a polysiloxane-polyol, dimethicone copolyol SF1488 from GE Silicones as a development-enhancer. Two plates were made, one containing 5% SF 1488 in the composition and a reference plate with no development-enhancer (Table 2).

The solutions were made in acetone: Dowanol PM, 75:25 at 10% solids. Plates were cast manually and baked at 130°C/3min. The coating weight was 1.8-1.85 g/m<sup>2</sup>. The plates were imaged at 12 W an energy series of 90-350 mJ/cm<sup>2</sup>. The plates were developed in Goldstar positive plate developer in a DuPont-Howson processor at

23°C and 30s passing time. Table 3 shows that SF1488 at 5% level brings a clearing point of 160mJ/cm<sup>2</sup> and a weight loss of 25% as compared to 320mJ/cm<sup>2</sup> and 20% for the reference.

5

Table 2

|                                    | Reference | Example 10 |
|------------------------------------|-----------|------------|
| Polymer1:Polymer 2, 46:54          | 86        | 82.5       |
| IR dye                             | 1         | 1          |
| Basic Blue 7                       | 8         | 6.5        |
| Tween-80                           | 5         | 5          |
| Dimethicone copolyol SF 1488       | -         | 5          |
| Clearing point, mJ/cm <sup>2</sup> | 320       | 160        |
| Weight loss in developer, %        | 20        | 25         |

#### Example 11:

10 This example presents a plate with two layers, the upper layer containing the light to heat converter.

Two coating solutions were prepared as follows.

15 Solution 1: Polymer 1: polymer 2, 1:1, 78%  
Hexyl resorcinol, 10%  
Basic Blue 7, 7%  
Tween-80, 5%

The solution was made in Dowanol PM at 10% solids.

20 Solution 2: 1 kg of phenol formaldehyde resin was prepared in-house having a phenol:formaldehyde molar ration of 0.9:1 using an acid catalyst, sulfuric acid. The resin solution had a pH=5 and a solids content of 10%. 1 g IR dye ADS 830WS was dissolved in 100 g ethanol and added under stirring to the phenol- formaldehyde resin solution.

25

Solution 1 was coated on anodized aluminum substrate by spraying . The coating weight was 1.6 g/m<sup>2</sup>. Solution 2 was then spray-coated on top of the coating from solution 1 giving an additional coating weight of 0.5 g/cm<sup>2</sup>. The resulting plate was baked at 125°C for 2.5 min. The plate was imaged at 830 nm with Creo's Quantum 800 imagesetter a series of energy density between 90-300 mJ/cm<sup>2</sup> and a power of 12 W. The plate was developed in a DuPont processor containing an alkaline developer made from a 7% sodium silicate solution of 66 mS/cm. The plate was developed for 30 s at 26°C. The plate had a clearing point of 150 mJ/cm<sup>2</sup> and a weight loss in developer of 20%.

10

There have thus been outlined the important features of the invention in order that it may be better understood, and in order that the present contribution to the art may be better appreciated. Those skilled in the art will appreciate that the conception on which this disclosure is based may readily be utilized as a basis for the design of other methods and apparatus for carrying out the several purposes of the invention. It is most important, therefore, that this disclosure be regarded as including such equivalent methods and apparatus as do not depart from the spirit and scope of the invention.

15